Decomposition of methyl orange using C_{60} fullerene adsorbed on silica gel as a photocatalyst *via* visible-light induced electron transfer

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ABSTRACT

Visible-light induced electron transfer reactions of C_{60} fullerene adsorbed on silica gel (C_{60}/SiO_2 powder) to methyl orange in water have been studied. The C_{60}/SiO_2 powder was simply prepared by mixing a toluene solution of the C_{60} fullerene with silica gel followed by evaporating the toluene. Irradiation by visible light (>420 nm) of the methyl orange aqueous solution (25 μM) in the presence of the C_{60}/SiO_2 powder and ascorbic acid resulted in the decomposition of the methyl orange. These results showed that the degradation conversion reached 96% after a 25-min visible light irradiation. The reaction also occurred by the irradiation of sunlight. The reductive products of methyl orange, *N,N*-dimethyl-*p*-phenylenediamine and sulfanilic acid, were ascertained and monitored by liquid chromatography/mass spectrometry (LC/MS). The reaction did not occur in the dark and in the absence of C_{60}/SiO_2 or ascorbic acid. The possible mechanism of the reaction is discussed. Furthermore, the C_{60}/SiO_2 powder was applied to a continuous flow system for the photodecomposition of methyl orange. C_{60}/SiO_2 powder was packed in a glass tube. The methyl orange solution was pumped into the glass tube, and the tube was irradiated by visible light or sunlight. The continuous decomposition of methyl orange was achieved by this method.

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1. Introduction

C_{60} fullerene has attracted special interest since its structure and properties are very unique [1,2]. In particular, the photoreactivity of C_{60} fullerene has received much attention because of its electron acceptability and broad absorbance in visible light region [3–5]. Intensive studies using C_{60} fullerene as a photocatalyst have been reported [6–9]. However, there are very few studies on the photoreaction of fullerene in water, because the compound shows a very low solubility in water (the aqueous solubility of C_{60}: 2.6–8.0 ng/L) [10].

It is very important for aquatic conservation to develop a visible-light induced reaction system, which can be applied to the decomposition of chemicals in water. There are several examples about the photoreaction of pollutants using C_{60} derivatives by the irradiation of visible light [11]. However, there are very few examples of useful reactions for water clean-up using C_{60} as a photocatalyst to the best of our knowledge [12].

In this report, we describe a novel photoreaction of methyl orange using C_{60} fullerene adsorbed on silica gel (C_{60}/SiO_2) and ascorbic acid *via* visible-light induced electron transfer. The surface of fullerene is hydrophobic, and C_{60} powder cannot disperse in an aqueous solution without several treatments, such as the evaporation of the tetrahydrofuran (THF)/water solution of C_{60} and hydroxylation of the surface [13,14]. C_{60} adsorbed on silica gel powder could disperse using a stirrer in the aqueous solution.

It has been reported that C_{60} adsorbed onto silica gel acts as a photocatalyst for the oxidation of olefins in acetonitrile [15,16]. However, to the best of our knowledge, there are no examples that C_{60} adsorbed onto silica gel has been applied to a visible light-activated photocatalyst for the decomposition of environmental pollutants in water. In addition, the photo-degradation of furfuryl alcohol in water by C_{60} immobilized on silica gel by amine–fullerene covalent binding has been reported [12]. It is well-known that the functional groups of fullerene affect the redox potential and reactivity of fullerene [17], and the photoreactivity of fullerene without functional groups in water has aroused considerable interest.

Methyl orange is one of the azo dyes, and it has been widely used as a model compound for the research of photoreactions [18]. Many

researchers have reported the decomposition of methyl orange using TiO_2 as a photocatalyst under ultraviolet irradiation [19–21]. However, there are few examples concerned with the decomposition of methyl orange by visible light irradiation [22]. In this study, we discuss the utility and mechanism of the degradation of methyl orange using C_{60}/SiO_2 as a visible light-activated photocatalyst. Furthermore, the C_{60}/SiO_2 powder was used in a continuous flow system for the photodecomposition of methyl orange with the objective to apply the photoreaction to water clean-up technology.

2. Experimental

2.1. Materials

C_{60} fullerene was obtained from SES Research (TX, USA). Methyl orange, ascorbic acid, acetonitrile (HPLC grade), 2-propanol, *tert*-butyl alcohol, acetic acid, ammonium acetate, sulfanilic acid, SiO_2 for column chromatography (particle diameter: 20–40 μm), *N,N*-dimethyl-*p*-phenylenediamine, and propham-$^{13}C_3$ were from Wako Pure Chemical Industries (Osaka, Japan). Toluene (HPLC grade) was obtained from Nacalai Tesque (Kyoto, Japan). Sodium dodecyl-d_{25} sulfate was obtained from CDN isotopes (Quebec, Canada). TiO_2 (JRC-TIO-4 (2)) was from AEROSIL (Tokyo, Japan).

Pure water was prepared using an automatic water distillation apparatus (MQ academic A10, Millipore, Billerica, MA, USA).

2.2. Preparation of the C_{60}/SiO_2 powder

The C_{60}/SiO_2 powder was prepared by a simple method using a rotary evaporator. The SiO_2 powder (1.0 g) was poured into the C_{60} toluene solution (30 mL, 133 μg mL^{-1}), and toluene was removed using a rotary evaporator. The obtained yellow powder was freeze-dried. In order to remove the fullerene, which is not steadily adsorbed on the silica gel, the powder was mixed with distilled water (40 mL) for 30 min followed by filtration, and freeze-dried again. The concentration of C_{60} adsorbed on the C_{60}/SiO_2 powder was determined by the toluene extraction. The absorbance of the extract was measured at 330 nm ($\log \epsilon = 4.38$ at 330 nm) [23]. As a result, 1.7 mg of C_{60} was adsorbed onto 1.0 g of the SiO_2 powder. When the powder (100 mg) was stirred in distilled water (10 mL) for 1 h, C_{60} was not detected in the supernatant (<0.01 μg/mL). This result indicated that desorption of C_{60} from the powder does not occur by mixing in aqueous solutions. The C_{60}/SiO_2 powder was investigated using a transmission electron microscope (JEM-2100, JEOL, Tokyo, Japan) and Raman microscope (inVia Reflex/StreamLine Plus 532/785, Renishaw, UK). The material was kept in the dark at room temperature, and used within a month of its production.

2.3. Preparation of the aqueous suspension of the nanoparticles of C_{60}

Deguchi et al. reported that the nanoparticles of C_{60} were obtained by hand-grinding the bulk solid of C_{60} fullerene [24]. We prepared a suspension of the nanoparticles of C_{60} obtained by hand-grinding. The hand-ground powder of C_{60} (20 mg) was mixed with distilled water (20 mL). The mixture was then sonicated and filtered using a membrane filter with the pore size of 0.45 μm (Millipore Corporation, Bedford, USA). The obtained suspension (C_{60} concentration, 5.6 μg mL^{-1}) was used as a photocatalyst. The particle size distribution of C_{60} in the suspension was measured by a dynamic light scattering method using Zetasizer Nano Series (Malvern Instruments Limited, Worcestershire, UK).

2.4. Photoreaction of methyl orange in the presence of the C_{60}/SiO_2 powder

Irradiation of the methyl orange aqueous solution (25 μM, 10 mL) containing ascorbic acid (0.50 mM) and the C_{60}/SiO_2 powder (20 mg) was carried out under an air or nitrogen atmosphere (N_2 bubbling:10 min) with a xenon lamp (300 W cm^{-2}) through a filter (>420 nm, L42, Hoya, Tokyo, Japan). The pH value of the solution was 4. The C_{60}/SiO_2 powder was dispersed in the reaction liquid by a stirrer bar during the photoreaction.

To investigate the reusability of the C_{60}/SiO_2 powder, the photodecomposition of methyl orange in water using the same C_{60}/SiO_2 powder was repeated. The suspension after the photoreaction was centrifuged (3000 rpm, 3 min), and the supernatant was removed from the tube and analyzed. The residue was mixed with the methyl orange aqueous solution in the presence of ascorbic acid, and irradiated again.

The reaction liquid was centrifuged at 3000 rpm for 3 min, and the UV spectrum of the obtained supernatant was analyzed by a UV absorption spectrometer (V-630, JASCO Corporation, Tokyo, Japan). The methyl orange concentration was analyzed by measuring its absorbance at 500 nm. The molar absorbance coefficient ϵ_m of the calibration curve was 3.1×10^4 L mol^{-1} cm^{-1} at pH 4. After the filtration of the reaction liquid using filter paper (No. 5A, Advantec, Tokyo, Japan), the solution was analyzed by electrospray ionization/mass spectrometry (ESI/MS) in both the positive and negative ion modes and liquid chromatography (LC)/MS for the detection and determination of its products. The reactions using sunlight were studied in the laboratory (Ueda City, Nagano, Japan). The solar radiation was monitored by 5 min by a photometer (TM-207, Tenmars Electronics, Taipei, Taiwan), and the values of the solar radiation in this study were around 600 W m^{-2}.

2.5. Photodecomposition of methyl orange by the continuous flow system

The C_{60}/SiO_2 column was prepared by putting 300 mg of C_{60}/SiO_2 powder into a pipette glass (4 mm inner diameter) stuffed with cotton. The length of the column was 2.5 cm. A methyl orange aqueous solution (25 μM) containing ascorbic acid (2.0 mM) was pumped through the C_{60}/SiO_2 column by a microtube pump (EYELA, Tokyo, Japan) at 0.70 mL min^{-1}. The solution was held in the column for 35 s. Irradiation of the column was carried out by a xenon lamp or sunlight. The eluent from the column was sampled and analyzed by UV absorption, ESI/MS and LC/MS.

2.6. ESI/MS analysis

The filtered sample solutions were analyzed by ESI/MS in the positive and negative ion modes. An LC/MS 2010 A mass spectrometer (Shimadzu, Kyoto, Japan) was used for the ESI/MS measurement. ESI/MS conditions were: scan range, m/z 50–500; heat block temperature, 200 °C; interface voltage, 4.5 kV; CDL voltage, 20 V. The solutions (10 μL) were injected into the LC/MS system, and the flow rate of the mobile phase (acetonitrile) was 0.20 mL min^{-1}.

2.7. LC/MS analysis

The filtered reaction solutions were analyzed using the LC/MS technique. The LC/MS 2010A was also used for the LC/MS measurement. An L-column ODS (Chemicals Evaluation and Research institute, Tokyo, Japan: 3 μm particle size, 2.1 × 150 mm i.d.) was used for the LC separation of the substrate and its products. The HPLC separation was carried out at 40 °C using a gradient composed of solution A (1.0 mM ammonium acetate solution) and solvent B (acetonitrile). The gradient conditions were as follows:
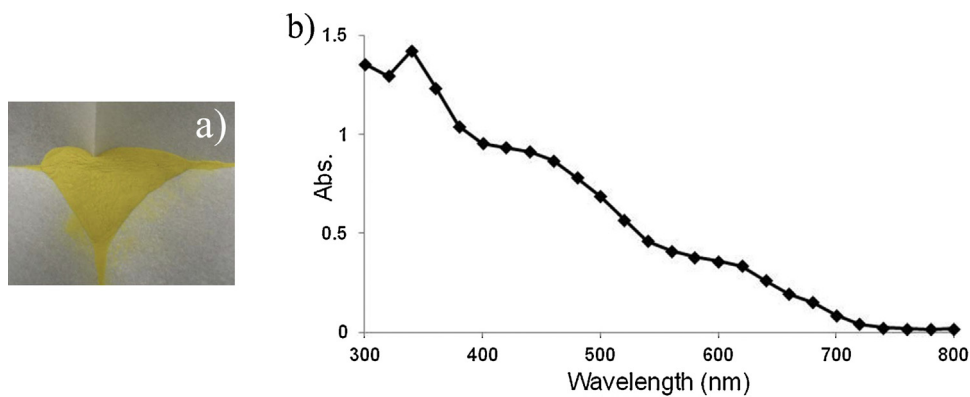
Fig. 1. (a) Photograph and (b) diffuse reflectance spectrum of C_{60}/SiO_2 powder (●: silica gel; ■: C_{60}/SiO_2).

0–5 min, hold at 2.5% B; 5–10 min, a linear increase from 2.5 to 5% B; 10–15 min, a linear increase from 5 to 99% B; 15–35 min, hold at 99% B. The flow rate was 0.20 mL min^{-1}. The ESI conditions were the same as described above. The sample solution (1.0 mL) was mixed with the internal standard methanolic solution (propham-$^{13}C_3$, 100 μg ml^{-1}; sodium dodecyl-d$_{25}$ sulfate, 100 μg ml^{-1}). The LC/MS acquisition was performed in the selected ion monitoring (SIM) mode at m/z 137 for N,N-dimethyl-p-phenylenediamine, m/z 172 for sulfanilic acid, m/z 187 for propham-$^{13}C_3$ and m/z 290 for sodium dodecyl-d$_{25}$ sulfate. The detection limits (S/N 3) were 0.01 and 0.005 μM for N,N-dimethyl-p-phenylenediamine and sulfanilic acid, respectively. The yields of the products were calculated based on the decomposed methyl orange.

3. Results and discussion

3.1. Characterization of C_{60}/SiO_2 powder

The C_{60}/SiO_2 powder was tinged with yellow (Fig. 1a). The diffuse reflectance spectrum is shown in Fig. 1b, and the result showed that the powder has an absorption band in the visible light region (400–700 nm). The Raman spectrum of the C_{60}/SiO_2 powder was very similar to that of the single-crystal C_{60} (Fig. S1) [25]. The strong line at 1468 cm^{-1} assigned to the A_g-pinch mode was observed. This result indicated that C_{60} fullerene in the powder adsorbs onto the silica gel without the formation of any covalent bonding.

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Fig. 2 shows a TEM image of C_{60}/SiO_2. Fullerene clusters around 500 nm were observed on the SiO_2. When the electron diffraction pattern of the adhesive cluster was measured, Debye–Scherrer rings were detected (Fig. S2). This result suggests that the fullerene cluster on the C_{60}/SiO_2 powder consists of many randomly-aligned micro-crystallites of C_{60}.

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The average zeta potential of C_{60}/SiO_2 was −9.43 mV at pH 4. This result suggests that the C_{60}/SiO_2 is distributed with a negative charge in water. On the other hand, the zeta potential of SiO_2 powder without treatment with C_{60} was −3.3 mV. Snow et al. reported that negatively-charged C_{60} cluster in aqueous water did not exhibit significant $^1O_2$ production by visible-light irradiation [26]. Therefore, it is expected that $^1O_2$ would not be produced by the C_{60}/SiO_2 powder under visible-light irradiation.
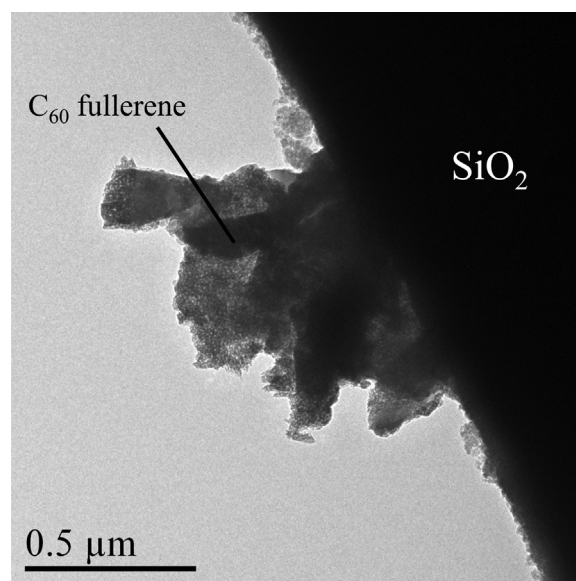

Fig. 2. TEM image of the C_{60}/SiO_2 powder.

3.2. Photodecomposition of methyl orange in the presence of C_{60}/SiO_2 powder

Methyl orange was not adsorbed by SiO_2 at pH 4. That makes easy to evaluate C_{60}/SiO_2 as a photocatalyst. In addition, SiO_2 does not disrupt the visible light absorption of C_{60}, because SiO_2 does not have an absorption band in the visible light region. Therefore, we selected SiO_2 as a support. The irradiation of a methyl orange solution containing the C_{60}/SiO_2 powder and ascorbic acid with a xenon lamp through a filter (>420 nm) resulted in the de-colorization of the solution due to the decomposition of methyl orange. Significant changes in the pH of the solution were not observed before and after the photoreaction. Methyl orange was not decomposed by the visible light irradiation without any additives. The photoreaction of methyl orange with C_{60}/SiO_2 in the absence of ascorbic acid also did not occur. The results are summarized in Table 1. Methyl orange was slightly decomposed in the presence of ascorbic acid without C_{60}/SiO_2 by the visible light irradiation (Table 1, entry 2). Photolysis of methyl orange under direct excitation occurred in the presence of ascorbic acid [27]. However, the efficiency of the reaction was significantly low compared to the reaction in the presence of C_{60}/SiO_2 (Table 1, entries 2 and 7). The conversion of methyl orange slightly decreased by the removal of oxygen (Table 1, entries 6 and 8 or entries 7 and 9). The adsorptive removal of methyl orange by the C_{60}/SiO_2 powder was not observed, when 20 mg of the C_{60}/SiO_2

Table 1
Photodecomposition (%) of methyl orange with C_{60}/SiO_2.[a]

Entry	Additives	Atmosphere	Light	Irradiation time (min)	Decomposition (%)
1	C_{60}/SiO_2	Air	Visible light (>420 nm)	25	0.80
2	Ascorbic acid (AA)	Air	Visible light (>420 nm)	25	4.0
3	None	Air	Visible light (>420 nm)	25	0.0
4	C_{60}/SiO_2	Air	Dark	25	0.40
5	C_{60}/SiO_2 + AA	Air	Dark	25	5.2
6	C_{60}/SiO_2 + AA	Air	Visible light (>420 nm)	15	85
7	C_{60}/SiO_2 + AA	Air	Visible light (>420 nm)	25	96
8	C_{60}/SiO_2 + AA	N_2	Visible light (>420 nm)	15	70
9	C_{60}/SiO_2 + AA	N_2	Visible light (>420 nm)	25	95
10	C_{60}/SiO_2 + AA + 2-propanol[b]	Air	Visible light (>420 nm)	15	73
11	C_{60}/SiO_2 + AA + 2-propanol[b]	Air	Visible light (>420 nm)	25	95
12	C_{60}/SiO_2 + AA + tert-butyl alcohol[c]	Air	Visible light (>420 nm)	15	68
13	C_{60}/SiO_2 + AA + tert-butyl alcohol[c]	Air	Visible light (>420 nm)	25	84
14	C_{60}/SiO_2 + AA	Air	Sunlight	15	86
15	C_{60}/SiO_2 + AA	Air	Sunlight	25	97
16	C_{60}/SiO_2 + AA	N_2	Sunlight	15	85
17	C_{60}/SiO_2 + AA	N_2	Sunlight	25	95
18	SiO_2 + AA	Air	Visible light (>420 nm)	25	4.0

[a] Initial concetrations of methyl orange and ascorbic acid were 25 mM and 0.50 mM, and the amount of C_{60}/SiO_2 powder was 20 mg/10 mL.

[b] The concentration of 2-propanol was 0.1 M. 2-propanol was used as a radical scavenger.

[c] The concentration of tert-butyl alcohol was 0.1 M. tert-Butyl alcohol was used as a radical scavenger.

powder was added to 10 mL of a methyl orange solution (25 μM, pH 4) in the presence of ascorbic acid (0.50 mM), and mixed by a magnetic stirrer for 160 min in the dark. In addition, methyl orange was slightly decomposed in the presence of ascorbic acid (2.0 mM) with the C_{60} powder (the average particle diameter: 110 μm, 3.4 mg in 10 mL) by the visible light irradiation. The decomposition of methyl orange was 7.2%. The decomposition (%) was lower than that using the C_{60}/SiO_2 powder. The result is due to the differences of the dispersibility and surface area between the C_{60}/SiO_2 powder and the C_{60} powder.

The effect of the ascorbic acid concentration on the decomposition of methyl orange was observed (Fig. S3a). Methyl orange was completely decomposed by the photocatalyst in the presence of ascorbic acid (>2.0 mM) under visible light irradiation for 15 min. The effects of the quantity of the C_{60}/SiO_2 powder on the decomposition (%) of methyl orange was also investigated (Fig. S3b). Methyl orange was efficiently decomposed in the presence of the powder (>20 mg/10 mL). Based on these results, it was found that the optimum concentrations of ascorbic acid and the C_{60}/SiO_2 powder were 2.0 mM and 20 mg/10 mL, respectively.

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Fig. 3 shows the temporal absorption changes of the filtered solution by the photocatalytic process. The plot of -ln C/C_0 versus time shows an approximate linearity, which indicated that the photoreaction of methyl orange with C_{60}/SiO_2 in the presence of ascorbic acid (0.50 mM) fitted a pseudo-first-order kinetic model (-ln C/C_0 = 0.0837 t, R^2 = 0.9949; Fig. 3).

The mass spectrum of the filtered solution after the irradiation (15 min) is shown in Fig. 4. The product of the photoreaction was assigned to N,N-dimethyl-p-phenylenediamine (**1**) based on ESI/MS and LC/MS measurements. The retention time of the product in the LC/MS measurement in the selected ion monitoring mode (m/z 137) was in agreement with that of the standard sample **1**, therefore, it was concluded that one of the products of this reaction was N,N-dimethyl-p-phenylenediamine. The ion peak at m/z 172 by ESI/MS in the negative ion mode also corresponded to the product of the photoreaction. The peak was assigned to sulfanilic acid (molecular weight: 173). The retention time of the product in the LC/MS measurement in the selected ion monitoring mode (m/z 172) was in agreement with that of the standard sulfanilic acid (**2**), and it was concluded that one of the products of this reaction
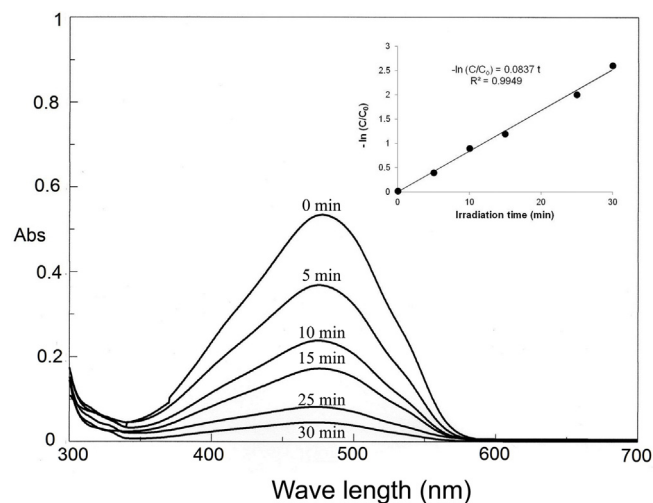
Fig. 3. UV spectral changes in the degradation of methyl orange by the photocatalytic process. Inset: Pseudo-first order plots of degradation of methyl orange vs. irradiation time. The initial concentrations of methyl orange and ascorbic acid were 25 μM and 0.50 mM, respectively. The sample volume was 10 mL, and the additive amount of the C_{60}/SiO_2 powder was 20 mg.

was sulfanilic acid. The yields of **1** and **2** were 88% and 55%, and the conversion of methyl orange was 96% (Table 1, entry **7**). The yield of **2** was low compared to the yield of **1** and the conversion of methyl orange. The result indicates that the product **2** underwent further reactions, and there are several products, which were not detected by ESI/MS. We also measured the filtered reaction solution by ion chromatography. As a result, the formations of NO_2^-, NO_3^-, and SO_4^{2-} were not observed. It is probable that the oxidation of ascorbic acid in the photoreaction results in the formation of dehydroascorbic acid as a similar photoreaction using ascorbic acid as an electron donor [28]. However, when the filtered solution after the photoreaction was injected into ESI source in the positive or negative ion modes, no ions assignable to dehydroascorbic acid were observed (Fig. 4 for the positive ion mode). It is possible that further reactions of dehydroascorbic acid occur and result in the formation of products that are not detected by ESI/MS.

The decomposition of methyl orange using the C_{60}/SiO_2 powder as a photocatalyst also occurred by the sunlight irradiation.

The decomposition (%) of methyl orange was 97% by the sunlight irradiation for 25 min (Table 1, entry 15).

The photodecomposition of methyl orange in water using the same C_{60}/SiO_2 powder was repeated five times to observe the reusability of the C_{60}/SiO_2 powder (Fig. S4). The decompositions (%) of methyl orange were over 95% and did not significantly decrease throughout the photoreaction cycles (1–5 times). Therefore, the C_{60}/SiO_2 powder can be repeatedly used as a photocatalyst to decompose methyl orange in water. This result suggests the possibility that the powder can be continuously use for a long period as a photocatalyst.

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3.3. Photodecomposition of methyl orange in the presence of the C_{60} nanoparticles

We prepared a suspension of the C_{60} fullerene nanoparticles, and studied the potential of the particles as a photocatalyst for the decomposition of methyl orange by visible light irradiation. The adsorption spectrum of the suspension of C_{60} was measured, and the suspension revealed absorption bands in the visible light region (400–700 nm) similar to those of the C_{60}/SiO_2 powder. The size distribution of the C_{60} particle in the suspension was 100–500 nm, and the average diameter was 192 nm. In the case of the visible light irradiation (2 h) of a methyl orange aqueous solution (4.2 mL) containing the C_{60} nanoparticles (16.8 μg) and ascorbic acid (2.0 mM), the decomposition of the methyl orange was observed. The decomposition (%) of methyl orange was 75%, which was lower than that using the C_{60}/SiO_2 powder as a photocatalyst. This result would be due to the quantity of C_{60} in the reaction system. Product **1** and **2** were also detected in the solution after irradiation, and the yields of **1** and **2** were 100 and 56%, respectively. Based on these results, it is suggested that the photocatalytic reaction using C_{60} nanoparticles is similar to that by the C_{60}/SiO_2 powder, and the efficiency of the photoreaction by C_{60}/SiO_2 is higher than that of C_{60} nanoparticles.

3.4. Mechanism of photodecomposition of methyl orange by the C_{60}/SiO_2 powder

The color of the methyl orange solution turned from orange to red by the addition of ascorbic acid, because methyl orange is protonated by the addition of ascorbic acid and forms the quinoid structure. The protonated methyl orange shows a stronger electron-acceptability compared to the neutral form of methyl orange. Recently, it was reported that methyl orange was decomposed into products containing *N,N*-dimethyl-*p*-phenylenediamine by visible light-irradiated natural sphalerite (conduction band: −1.4 V vs SCE; E_g: 2.95 eV) in the presence of ascorbic acid (the oxidative potential: 0.127 V vs NHE) [28]. The mechanism of the

reaction was proposed as follows: methyl orange (the reduction potential: −(0.058 pH) V vs. SCE) was reduced by the excited-state natural sphalerite, and destruction of the azo bond resulted in the formation of **1**.

Based on the photoreaction using natural sphalerite and the results from the present photoreaction of the C_{60}/SiO_2 powder, we have proposed a possible mechanism for the photoreaction of methyl orange as shown in Fig. 5. The first step is the photoexcitation of the C_{60} fullerene on the surface of the C_{60}/SiO_2 powder. It has been reported that the triplet state of C_{60} fullerene is formed with a quantum yield of 1.0 [29], and it is probable that the excited C_{60} fullerene on the surface of the C_{60}/SiO_2 powder undergoes an inter-system crossing from the singlet to triplet state. In addition, it was reported that $E_{red}(C_{60})$ was −0.42 V (vs SCE, solvent benzonitrile) and $E_S(^1C_{60}) = 1.9$ eV [29,30]. The next step is the electron transfer from the excited C_{60} to the protonated methyl orange (quinoid structure) and from ascorbic acid to the excited C_{60}. The radical species of methyl orange undergo bond cleavage to generate the product **1**. The efficiencies of the reaction at pH 6–10 were significantly low compared to the reaction at pH 4 (decomposition (%) of methyl orange at pH 6 was 4.8%). These results support the proposed mechanism.

It has been reported that the irradiation of C_{60} fullerene forms reactive oxygen species in the presence of oxygen [31,32]. This pathway leads to the electron transfer from donors to the excited-state C_{60}, forming the C_{60} radical anion [29]. Next, the superoxide anion radical ($O_2{}^{\bullet-}$) can form *via* O_2 receiving the electron from $C_{60}{}^{\bullet-}$.

The decomposition (%) of methyl orange slightly decreased by the removal of oxygen (Table 1, entries 6 and 8 or entries 7 and 9). This result would be caused by the reaction of methyl orange with the superoxide anion radical formed by electron transfer between the C_{60} radical anion and oxygen.

The addition of 2-propanol slightly decreased the decomposition (%) of methyl orange (Table 1, entries 6, 7, 10 and 11). Furthermore, for the addition of *tert*-butylalcohol, the decomposition (%) of methyl orange also decreased (Table 1, entries 6, 7, 12 and 13). These results also indicated that the formation of the superoxide anion radical affects the photodecomposition of methyl orange [33].

Recent study has suggested that the photoinduced electron transfer from a photoexcited dye to TiO_2 by the irradiation of visible light lead to the decomposition of the dye [34]. Methyl orange was not decomposed by the visible light irradiation (15 min) of a methyl orange aqueous solution (pH 4) containing C_{60}/SiO_2 in the absence of ascorbic acid. The pH value of the aqueous solution was adjusted by HCl. This result indicates that the photodecomposition of methyl orange is not occurred by only effect of pH change, and the reaction does not proceed without ascorbic acid. Furthermore, methyl orange was not decomposed by the visible light irradiation of a methyl orange solution (pH 4) containing TiO_2 in the absence
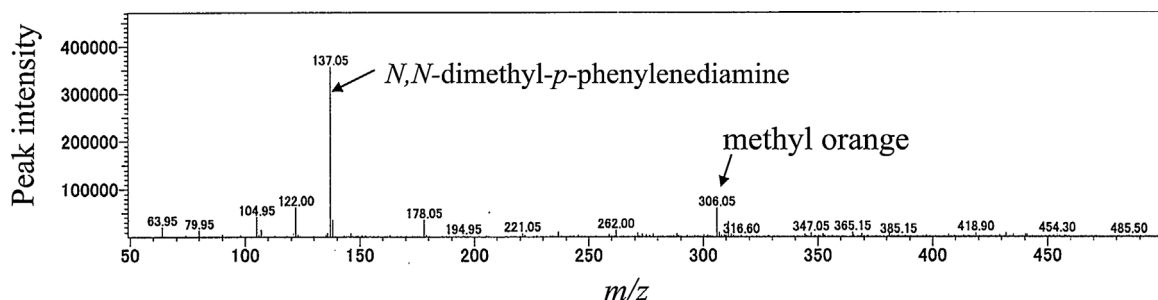

Fig. 4. Mass spectrum of the filtered solution after the photoreaction of methyl orange with C_{60}/SiO_2 powder for 15 min (ESI in the positive ion mode). The initial concentrations of methyl orange and ascorbic acid were 25 μM and 0.50 mM, respectively. The sample volume was 10 mL, and the amount of C_{60}/SiO_2 powder was 20 mg.
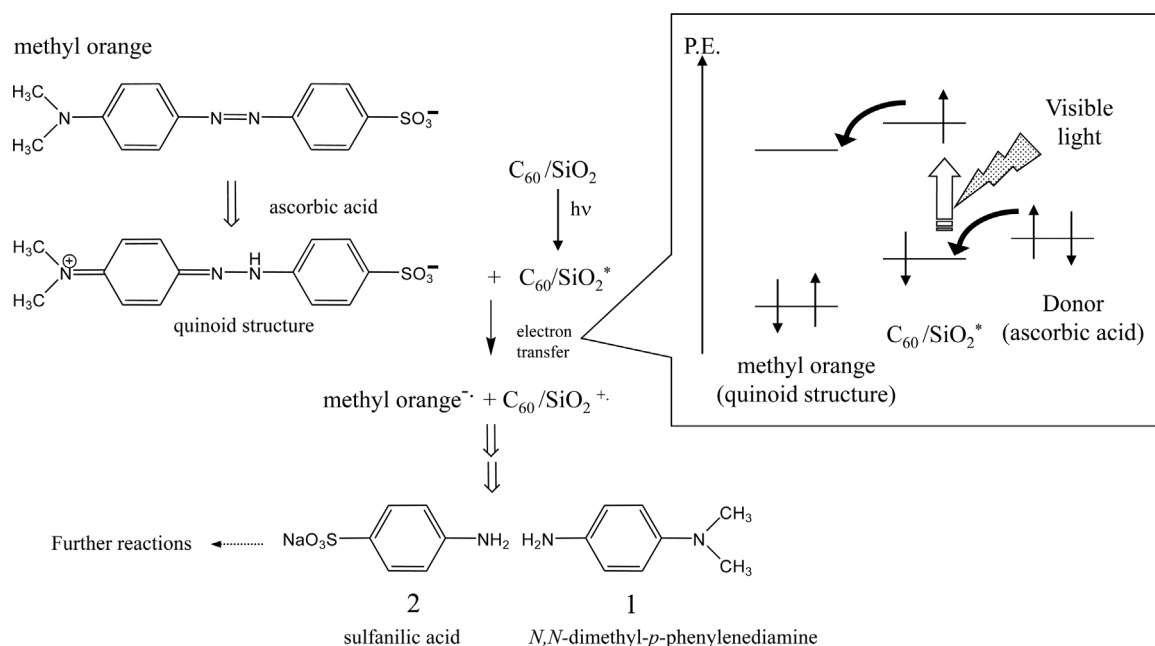
Fig. 5. A possible mechanism for the photodecomposition of methyl orange in the presence of aqueous C_{60} cluster.
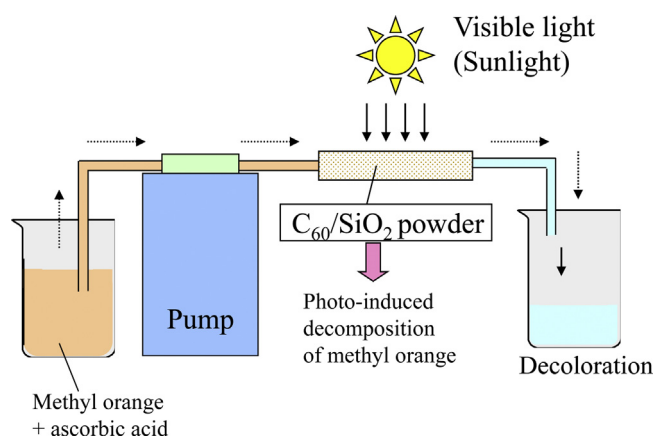

Fig. 6. An outline of the continuous flow system for the photo-decomposition of methyl orange by the C_{60}/SiO_2 powder.

of ascorbic acid. In the case of the irradiation of sunlight (15 min), methyl orange was decomposed by using TiO_2 as a photocatalyst in the absence of ascorbic acid (pH 4, decomposition (%): 28.6%). The photodecomposition of methyl orange would be induced by the ultraviolet radiation of sunlight. In addition, an earlier study has shown that mixing TiO_2 with ascorbic acid resulted in the formation of charge-transfer bidenate complex [35].

3.5. Continuous flow system of photodecomposition of methyl orange using C_{60}/SiO_2 packed column

With a aim to apply the C_{60}/SiO_2 powder as the photocatalyst for water clean-up, a continuous flow system for the photoreaction of methyl orange with the C_{60}/SiO_2 powder was studied. Fig. 6 is a schematic of the continuous flow system for the photodecomposition of methyl orange by the C_{60}/SiO_2 powder. The conditions for the system, such as the flow rate of the sample solution, and continuous reaction time, were changed, and the changes in the decomposition (%) of methyl orange were investigated.

The continuous decolorization of the sample solution was achieved by the visible light irradiation. When the initial concentra-

tion of ascorbic acid in the solution was 2.0 mM, the decomposition (%) of methyl orange was around 90% at the flow rate 0.70 mL min^{-1} by the photoreaction for 1 h. Products 1 and 2 were detected in the solution under the continuous flow condition. The decomposition of methyl orange through the column did not occur in the dark. The mobile phase passed through the column in 35 s at this flow rate. The continuous decomposition of methyl orange was achieved, because the reaction of methyl orange by photoinduced electron transfer with the C_{60}/SiO_2 powder is very rapid. When the flow rates were 1.1 or 1.4 mL min^{-1}, the decompositions (%) of methyl orange were 88 and 74%, respectively. The decrease in the decomposition (%) of methyl orange compared to the flow rate at 0.70 mL min^{-1} would be due to the insufficient holding time of methyl orange in the column.

A similar reaction occurred by the sunlight irradiation (the decomposition (%) of methyl orange: 89% at the flow rate 0.80 mL min^{-1}). This result indicated that the present method is useful as a novel water clean-up technology without using fossil energy.

4. Conclusion

The irradiation of visible-light led to the decomposition of methyl orange using C_{60}/SiO_2 powder in the presence of ascorbic acid. The reaction also occurred by the irradiation of sunlight, therefore, indicating that the C_{60}/SiO_2 powder could be used as a novel sunlight-sensitized photocatalyst for the decomposition of pollutants.

No additional reactions of the products (1 and 2) were observed under the condition described above. The development of the method to mineralize the products is needed together with the establishment of the presented method.

In this study, the detachment of C_{60} from the C_{60}/SiO_2 powder was not confirmed. However, there is the possibility that the fullerene cluster is desorbed using the powder for a long time. The toxic effects of fullerene on aquatic organisms have been extensively studied in order to understand its environmental risk when used. For example, Oberdörster reported the toxicity of C_{60} cluster dispersed in water for fish [36]. However, in most of these studies, there is the possibility that the test solution contains a trace amount

of THF, which was used for the preparation of the particle, and the residual THF is related to the toxic effects of the C_{60} cluster. In fact, Deguchi et al. reported that C_{60} nanoparticles prepared without THF or other organic solvents revealed no toxic effects on the growth of *Escherichia coli* (the concentration of C_{60} in a nutrient-poor minimal Davis medium: 5 $\mu g\,mL^{-1}$ of C_{60} nanoparticle) [24].

In order to evaluate the utility of the C_{60}/SiO_2 powder, it is important to study the decomposition of other environmental pollutants by the C_{60}/SiO_2 powder as a photocatalyst. We have already confirmed that methyl red was decomposed by C_{60}/SiO_2 powder under the same condition described above. In addition, further studies on the influences of various environmental matrices on the reaction using the C_{60}/SiO_2 powder are needed. We observed the photodecomposition of methyl orange in seawater using the C_{60}/SiO_2 powder. The sunlight irradiation to a methyl orange seawater solution (25 μM) in the presence of the C_{60}/SiO_2 powder (20 mg) and ascorbic acid (5.0 mM) resulted in the decomposition of methyl orange. The decomposition (%) of methyl orange was 93% by the irradiation of sunlight for 10 min.

Furthermore, the necessity of ascorbic acid for the reaction is questionable from the viewpoint of water purification because of cost-effectivity and the load of ascorbic acid to environment. The next step in this study is to develop the photoreaction system of the C_{60}/SiO_2 powder using other compounds instead of ascorbic acid as an electron donor.

Acknowledgements

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